

CHEMOCHROMIC HYDROGEN SENSORS

Bryan C. Wiggins
John Kennedy Space Center
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Reviewed by NASA Mentor
Janine Captain, Ph.D.
Applied Technology, KT-D-2

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A note to the reader:

Bryan Wiggins completed a successful summer research project at KSC working on chemochromic sensors. He contributed to the progress of the project and put significant effort into staying on schedule and learning as much as he could during his time here. This paper reflects only a small portion of the work that Bryan did during his internship at KSC because of the nature of the project. We are working to file patents on some of the materials Bryan was working with and other portions of the work dealt with IP sensitive material which could not be disclosed here. If any further information is needed please don't hesitate to contact me.

Janine Captain
Janine.E.Captain@nasa.gov

ABSTRACT

As fossil fuel supplies decline, hydrogen is quickly becoming an increasingly important fuel source. Currently hydrogen is the prime fuel of today's space vehicles (e.g., Space Shuttle) and featured as a fuel for some prototype vehicles such as the BMW seven series model. Hydrogen is a colorless, odorless gas with a 4% lower explosive limit which makes leak detection a priority.

In an effort to support the use of hydrogen, a chemochromic (color changing) sensor was developed that is robust, simple to use, and does not require active operation. It can be made into a thin tape which can be conveniently used for leak detection at flanges, valves, or outlets. Chemochromic sensors can be either reversible or irreversible; however, irreversible chemochromic sensors will be analyzed in this report. The irreversible sensor is useful during hazardous operations when personnel cannot be present. To actively monitor leaks, testing of the irreversible sensor against environmental effects was completed and results indicated this material is suitable for outdoor use in the harsh beachside environment of Kennedy Space Center. The experiments in this report will give additional results to the environmental testing by adding solid rocket booster residue as a variable. The primary motivation for these experiments is to prepare the sensors for the launch pad environment at the Kennedy Space Center. In an effort to simulate the atmosphere at the pads before and after launch, the chemochromic sensors are exposed to solid rocket residue under various conditions.

INTRODUCTION

Hydrogen sensors are subject to interference, and many require an operator to control the device. Because hydrogen leaks can create a hazardous environment, a remote sensor would be beneficial. Hydrogen fuel is becoming more and more popular as fossil fuel supplies are declining. In an effort to help ensure a safe environment when using this highly explosive gas, a chemochromic sensor is under development that provides rapid response in the presence of hydrogen.

The sensors are especially designed to be robust and to fit into small areas where leaks may occur. There are numerous pipe lines that transport hydrogen throughout the launch pads. In several areas the connection points are in tight spots and hard-to-view areas for operators and via cameras. With hydrogen being a colorless gas, it is quite difficult to detect leaks and some leaks may go unnoticed. The sensor was made with a special matrix that goes through a chemical reaction that causes a change in color when exposed to hydrogen. Because of the color changing phenomenon, the sensor can be left during hazardous operations and does not require any power or operator actions. This is especially important in hydrogen transportation, loading, and storage due to the low flammability limit of hydrogen.

EXPERIMENT

The experiments were performed on three different sensor formulations. There were four different treatments per formulation, and three different tests were performed to each treatment. There was a control sample (C) that consisted of no treatment, a one hour treatment (SH) which was exposed to solid rocket booster residue (SRB) for an hour, a three day treatment (SD) which was exposed to SRB residue for three days, and a week treatment (SW) which was exposed to SRB residue for a week. The solid rocket residue was simulated by making a slurry that consisted of 6.60 mL hydrochloric acid of approximately 0.1 pH, 100mL of deionized water, and 5.60 grams of alumina oxide powder. The final pH was approximately of 0.25.

All the samples were analyzed for their response to hydrogen and tested for strength. An additional test for reaction with hydrogen was done after environmental exposure had taken place for one week. Each sample was exposed to 100% hydrogen in a hydrogen (H₂) exposure chamber for 15, 30, and 60 seconds. The volume of the chamber was approximately one liter; the flow through the chamber was approximately 398 sccm. The second test was the durability of the chemochromic tapes. The environmental exposure took place at the KSC corrosion beach site. At the beach site, tapes were exposed to atmospheric conditions located approximately 100 feet from the Atlantic Ocean. Individual pieces were attached to a stainless steel panel, and the panels were placed on racks. The racks are 5 feet high and oriented 60° from the plumb line. The samples were transported back in the laboratory and exposed to 100% hydrogen the same way as the previous test. An Instron was used to calculate the tensile strength and modulus of each type of sample. The samples were cut out into unique dog bone shapes using a manual punch. More details on how the tensile strength was obtained will be discussed later in the paper.

RESULTS AND DISCUSSIONS

After the hydrogen exposures, the color change was measured using a Konica Minolta CR-400 chroma meter. The instrument gives a ΔE value when measuring the samples. ΔE measures a difference in color by measuring specific parameters of the film (L^* , a^* , and b^*). L^* refers to a gradient from light to dark; a^* defines the gradient from red to green; and b^* the gradient from yellow to blue. The total color difference, ΔE , is calculated using the L^* , a^* , and b^* values measured for the two colors being compared. It is defined by the equation:

$$\Delta E = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \quad (\text{Equation 1})$$

The greater the ΔE value, the greater the color contrast. There was a control sample for each exposure so the extent of color change could be measured. The longer the tapes were exposed to hydrogen the greater the ΔE . It appears the longer the tapes were

submerged in the SRB residue the faster they reacted with hydrogen. Below, Figure 1 shows a graph of the ΔE versus time of the S2 sample. As the time increases the contrast of color does also.

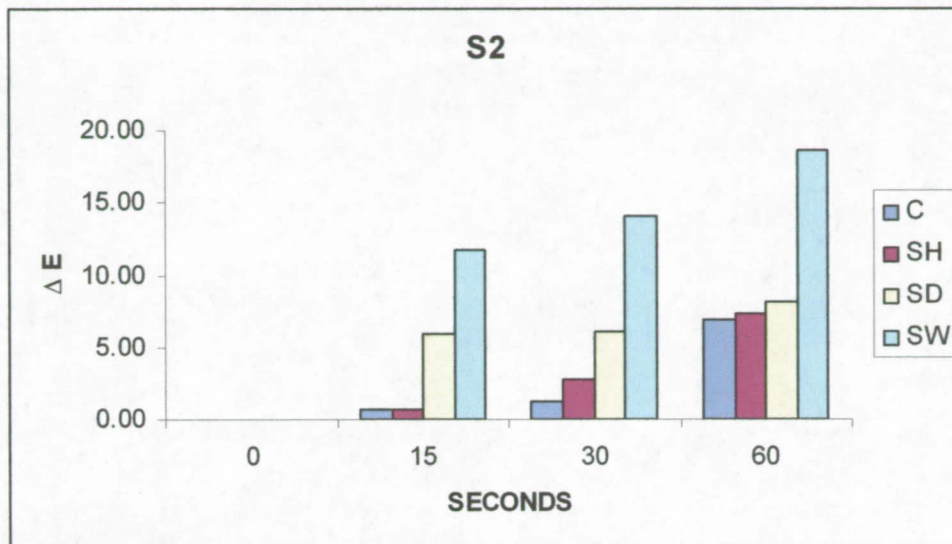


FIGURE 1. S2 exposure test

The solid rocket booster residue enhances the response time but seem to distort the sensor if it is not rinsed with DI water after submersion. The material will fade to a pale grayish color with an average ΔE of 16.60.

The beach site test went as planned, but the results were somewhat unexpected. The beach site exposure corrupted several of the sensors. All of the samples that were previously submerged in SRB residue and controls were altered. The samples started to change color before H_2 testing. Several of sensors were completely changed, whereas others were slightly spotted. The beach site samples responded to H_2 faster then the sample that had no environmental exposure. The comparison of S1 and EV controls for the exposure and the controls for the beach site test are shown in Figure 2.

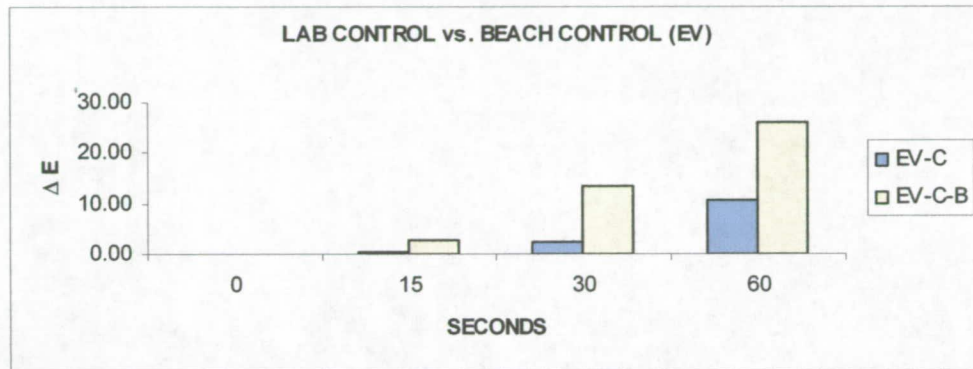
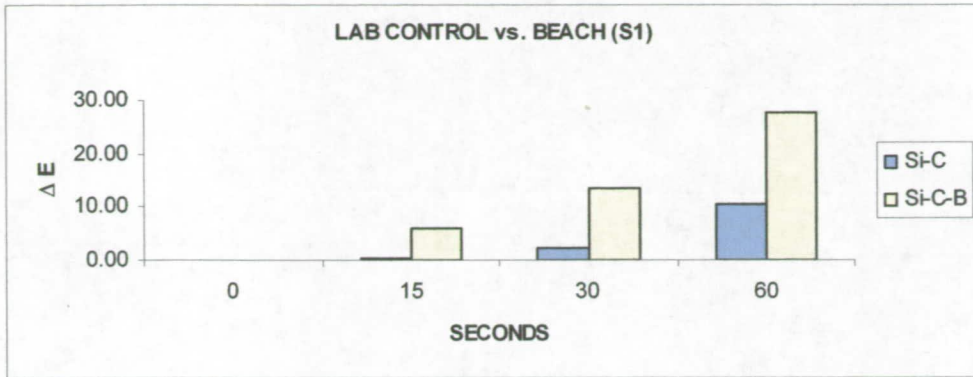


FIGURE 2. Lab control vs. beach control

The beach site environment had a substantial effect on the sensor. More research will need to be done to determine the mechanism that caused this change.

The tensile strength test was the final test done on the samples. This test was performed to determine if the SRB exposure affected the strength of the polymer. The Instron clamped onto the end of the bones-shaped samples then stretched the sample until it broke. The amount of force was measured by the machine as it stretched the sample. The force was divided by the cross-sectional area which gave the stress that the sample is experiencing.

$$\text{Force} / \text{Area} = \text{Stress} \quad (\text{Equation 2})$$

The force was increased as the sample stretched which caused the stress to increase until the sample broke. The stress needed to break the sample is referred to as the tensile strength. The modulus was also calculated by the Instron test. The modulus is the ability the sample has to resist deformation. Modulus is usually expressed as the ratio of stress exerted on the sample to the amount of deformation. Tensile modulus is the ratio of stress applied to the elongation which results from the stress. Therefore the modulus is the slope of the stress-strain curve.

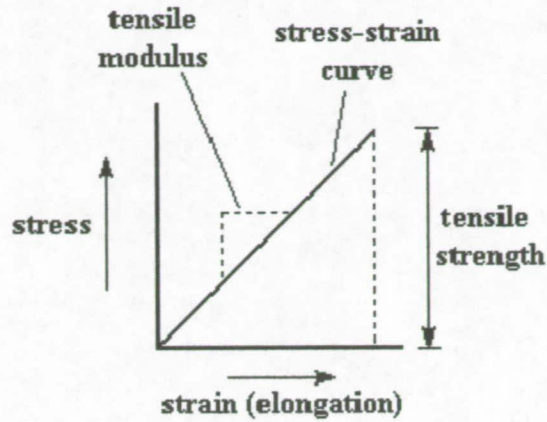


FIGURE 3. Stress strain curve

The area under the stress-strain curve is the toughness of the material. Toughness is the amount of energy the sample can endure before it breaks. Toughness is different from strength. If the sample is tough, it does not mean it is strong. The plot below describes the relationship between toughness and strength.

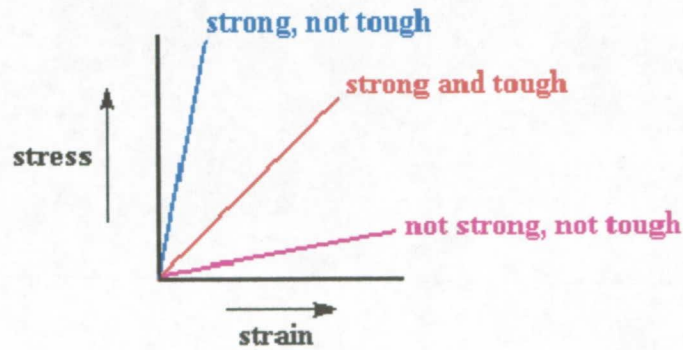


FIGURE 4. Characteristic toughness and strength results

The SRB residue or the beach exposure did not have a significant affect on the sample during the Instron testing. The sensors maintained their mechanical integrity throughout the tests.

CONCLUSIONS

Synthesis of the chemochromic hydrogen sensor was performed to create a set of samples for testing. The SRB residue enhanced the response of the sensor without affecting the sensor modulus or tensile strength when the sample was rinsed after SRB exposure. SRB exposure did cause some degradation of the sensors when it was allowed to dry without rinsing. When the sensor was exposed to the beach site for a week the samples were altered. The chemochromic sensors have previously been tested in outdoor environments, but they have never been tested with SRB residue in an outdoor environment. It appears that leaving the SRB residue on the sample degrades the sensor.